Photocatalytic reduction of [RhCl$_n$(H$_2$O)$_{6-n}$]$^{3-n}$ ($n = 0$–6) in a titanium dioxide suspension: The role of structurally different sacrificial reducing agents

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ABSTRACT

The photocatalytic reduction of rhodium(III) chloro–aqua complexes, [RhCl$_n$(H$_2$O)$_{6-n}$]$^{3-n}$ ($n = 0$–6), was carried out employing formic acid, ethanol and sucrose as hole scavengers or sacrificial reducing agents (SRA). The investigation was conducted in air equilibrated titanium dioxide (TiO$_2$) suspensions at 25 °C and pH 1 employing UV light within a closed-loop flow-through reactor. Varying the sodium chloride concentration, according to speciation data, individual solutions of rhodium(III) chloro–aqua complexes were prepared at those Cl$^-$-concentrations coinciding with the maximum of a specific species, and to that regard the photocatalytic reduction behaviour of Rh(III) was related to the complex present in greater abundance. The fastest photocatalytic reduction rate was observed for those solutions having neutral and anionic rhodium(III) chloro–aqua complexes dominant in solution. No photocatalytic reduction, of any of the rhodium(III) chloro–aqua complexes, was effected in the absence of an organic SRA, which is in contrast to [PdCl$_n$(H$_2$O)$_{4-n}$]$^{2-n}$ ($n = 0$–4) and [PtCl$_n$(H$_2$O)$_{4-n}$]$^{2-n}$ ($n = 0$–4) that do show photocatalytic reduction in the absence of an added organic SRA. At low concentrations sucrose was found to be a superior SRA compared to both ethanol and formic acid. This behaviour is attributed to the structural differences of the SRAs as sucrose has more oxidizable electron donor sites, in the form of hydroxyl groups, compared to both ethanol and formic acid. However, at higher concentrations ethanol was found to be a more effective SRA than both formic acid and sucrose. This is due to coagulation of the photocatalyst (TiO$_2$) setting in at higher sucrose concentrations, which causes the photocatalyst to settle out from suspension.

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1. Introduction

1.1. Background

Platinum group metals (PGMs) are primarily extracted from ores, but due to their high value they are also secondarily recovered from industrial residues like automotive catalysts and spent industrial catalysts of variable composition and quality. The development of new technologies for the extraction, recovery and separation of these metals is therefore of special interest. Current recovery and separation processes are quite complex and involve many steps such as solvent extraction, ion exchange, precipitation, crystallization and distillation [1–3]. As a result of such recovery activities waste waters containing small amounts (in ppm range) of PGMs

are produced annually from PGM ore process plants and from the recovery of these precious metals from secondary sources. Ecological concerns, e.g. water pollution by these metals, are crucial and can have a great effect on production costs. Considerations such as these have led to the investigation of cleaner recovery methods for small amounts of PGMs in waste water streams. One such a technique is TiO$_2$ semiconductor photocatalysis that not only finds application in the photocatalytic oxidation of organic pollutants [4–6], but can also be applied towards the development of photocatalytic reduction processing techniques that are environmentally safe. Several articles [7–9] have been published on the recovery of these metals employing photocatalysis, but these articles hardly ever mention speciation as a parameter to be considered. Speciation, which provides the distribution of the rhodium(III) chloro–aqua complexes as a function of chloride concentration, has been discussed in detail in literature [10–13]. These literature references describe the challenges posed by these complexes if one needs to apply, for example, solvent extraction as a

Table 1
Overall formation constants ($\log \beta_n$) for the $[RhCl_n(H_2O)_{6-n}]^{3-n}$-system ($n = 1$–6) [10].

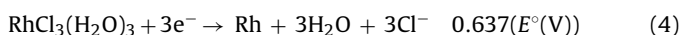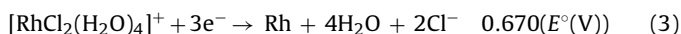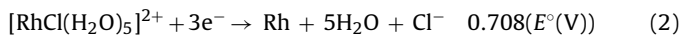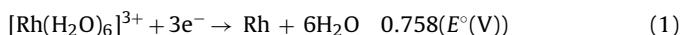| $[RhCl_n(H_2O)_{6-n}]^{3-n}$	$\log \beta_n$
$[RhCl(H_2O)_5]^{2+}$	2.49
$[RhCl_2(H_2O)_4]^+$	4.45
$RhCl_3(H_2O)_3$	6.14
$[RhCl_4(H_2O)_2]^-$	7.61
$[RhCl_5(H_2O)]^{2-}$	8.11
$[RhCl_6]^{3-}$	7.82

method of rhodium recovery from a chloride solution. The challenges include formation of two or more rhodium(III) chloro–aqua complexes with different properties of extractability, formation of chloro–hydroxo complexes if the pH is not maintained at 1 or below and formation of rhodium(III) chloro dimers such as $Rh_2Cl_9{}^{3-}$. Kinetic studies of ligand substitution reactions of the rhodium(III) chloro–aqua complexes have also been extensively investigated in literature [14–18] and references therein. It has been shown that both $[PdCl_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4) [19] and $[PtCl_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4) [20] can be successfully reduced photocatalytically in the absence of an added SRA for $n = 0$–3. We report here on the recovery of rhodium(III) from solutions of its chloro–aqua species by photocatalytic reduction in a titanium dioxide suspension. The photocatalytic reduction trends of $[RhCl_n(H_2O)_{6-n}]^{3-n}$ ($n = 0$–6) complexes by UV illumination in a suspension of titanium dioxide were studied in the absence of an added SRA as well as in the presence of formic acid, ethanol, and sucrose as SRAs.

1.2. Thermodynamics of $[RhCl_n(H_2O)_{6-n}]^{3-n}$ ($n = 0$–6) species in aqueous solution

The extent of the removal of different rhodium ions (complexed with the same ligand) from solution, by photocatalytic reduction, has not been investigated systematically. Levitin et al. [13] computed the fractional percentage of Pt, Pd and Rh as a function of chloride concentration and constructed distribution graphs that he used for solvent extraction as a means of noble metal recovery from solution. A similar approach to that employed by Levitin and co-workers, for the stepwise reaction between Rh and chloride ligands, was applied in this study and the log β-values used (Table 1) were those reported in literature [10]. Applying the Nernst equation to calculate the $E°$-values from the log β-values for the individual half-reactions (Eqs. (1)–(7)), it is seen that there is a general decrease in the $E°$-values with higher coordination of Cl^-. This decrease is however not so marked for the anionic rhodium(III) chloro–aqua complexes compared to the cationic complexes, which can be directly linked to their log β-values (Table 1, Section 2.2). From the trends shown by the standard reduction potentials (Eqs. (1)–(7)) it is deduced that the cationic complexes should be easier to reduce than the anionic complexes.

$$[Rh(H_2O)_6]^{3+} + 3e^- \rightarrow Rh + 6H_2O \quad 0.758(E°(V)) \tag{1}$$

$$[RhCl(H_2O)_5]^{2+} + 3e^- \rightarrow Rh + 5H_2O + Cl^- \quad 0.708(E°(V)) \tag{2}$$

$$[RhCl_2(H_2O)_4]^+ + 3e^- \rightarrow Rh + 4H_2O + 2Cl^- \quad 0.670(E°(V)) \tag{3}$$

$$RhCl_3(H_2O)_3 + 3e^- \rightarrow Rh + 3H_2O + 3Cl^- \quad 0.637(E°(V)) \tag{4}$$

$$[RhCl_4(H_2O)_2]^- + 3e^- \rightarrow Rh + 2H_2O + 4Cl^- \quad 0.608(E°(V)) \tag{5}$$

$$[RhCl_5(H_2O)]^{2-} + 3e^- \rightarrow Rh + H_2O + 5Cl^- \quad 0.598(E°(V)) \tag{6}$$

$$[RhCl_6]^{3-} + 3e^- \rightarrow Rh + 6Cl^- \quad 0.604(E°(V)) \tag{7}$$
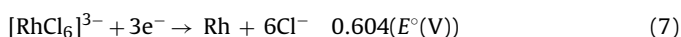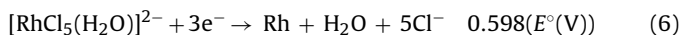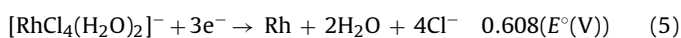
1.3. The photocatalytic redox principle

When titanium dioxide, with specific reference to the anatase crystal structure, is illuminated with UV light of wavelength $\lambda \leq 388$ nm, photons greater than or equal to its band gap energy of 3.23 eV are absorbed and electron–hole pairs are generated within the photocatalyst. The generated electrons are excited into the conduction band, while the holes remain in the valence band. These photo-generated electron–hole pairs facilitate redox reactions on the TiO_2 surface. The photocatalytic activity of TiO_2 depends on the relative rates of generation and recombination of these electron–hole pairs. To maintain charge separation, and thereby making the electrons in the conduction band available for the reduction of chloro–aqua rhodium(III) complexes, an easily oxidizable SRA is required. A number of papers discussing the type and role of SRAs in the photocatalytic reduction of metal pollutants have been published [21–24]. Kriek et al. [7] and Borgarello et al. [9] investigated certain aspects of the photocatalytic reduction of rhodium(III) chloro–aqua complexes (at high Cl^--concentrations) employing methanol, ethanol and sucrose as SRAs. The concentration of methanol [9] ranged from 2.47 to 4.94 mol l^{-1}, while the concentration of sucrose, in a 500 ml suspension of Rh(III) and Pd(II) ions, was 6.0×10^{-4} mol l^{-1} [7]. No photocatalytic reduction of Rh(III) ions was observed at this concentration while Pd(II) ions were reduced thereby effecting the photocatalytic separation of the two metals from solution. However, when ethanol was used as SRA the rate of photocatalytic reduction of Rh(III) was observed to be faster at concentrations above 0.01 mol l^{-1} and a 0.13 mol l^{-1} ethanol concentration was subsequently used as standard for further recovery and separation of the PGMs [7]. Matthews [25] employed formic acid, ethanol, and sucrose among other SRAs, with their concentrations ranging from 2.92×10^{-6} to 2.17×10^{-3} mol l^{-1}.

2. Experimental

2.1. Reagents

Anionic complexes of Rh(III) were prepared from $RhCl_3.3H_2O$ (>99.99% purity, Ultraspec) by dissolving the salt in 3 M $HClO_4$ (70% w/w in water from Merck (Pty) Ltd) so as to produce the desired stock solution. It was necessary to work with a high $HClO_4$ concentration (≥ 2 M) to prevent hydrolysis of the rhodium(III) chloro–aqua complexes to rhodium(III) hydroxo complexes and also to prevent the polymerization of these complexes [14]. The cationic rhodium(III) chloro–aqua complexes were prepared from $Rh(NO_3)_3 \cdot 3H_2O$ (Heraeus Chemicals). NaCl (Sigma-Aldrich) of 99.8% purity was used to prepare the individual rhodium(III) chloro–aqua complexes while $NaClO_4.H_2O$ (Sigma-Aldrich) was used to adjust the ionic strength of the solutions. Deionised water from a Millipore Milli-Q system was used to prepare all solutions. Evonik Degussa P25 (85.3% anatase and 14.7% rutile, with a BET surface area of 50.5 m^2 g^{-1}) was used as photocatalyst and its amount in suspension was 2 g l^{-1}. Absolute ethanol was sourced from Sigma–Aldrich, while formic acid (99%) was acquired from Merck (Pty) Ltd. The sucrose employed was the normal white table sugar. The concentration of the SRAs employed was either 0.01 mol l^{-1} or 0.1 mol l^{-1} in 500 ml reaction solutions. The initial Rh(III) concentration for all photocatalytic runs was 50 ppm (4.86×10^{-4} mol l^{-1}) in 500 ml.

2.2. Speciation of rhodium(III) chloro–aqua complexes

The stability constants (formation constants, [10]) used to prepare individual solutions of the rhodium(III) chloro–aqua complexes are listed in Table 1.
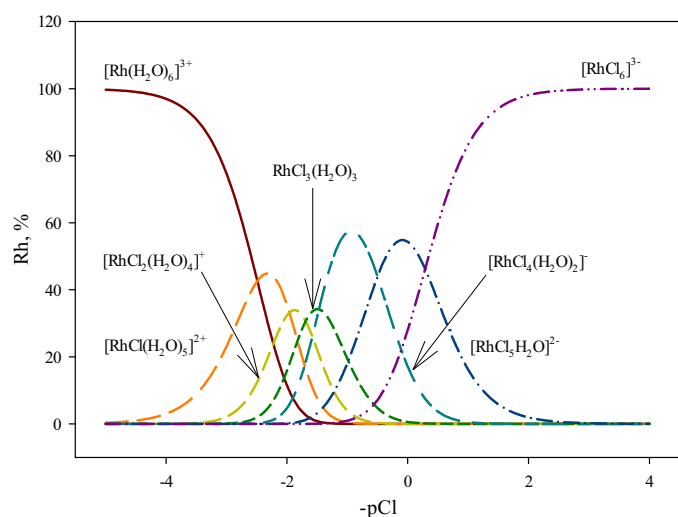
Fig. 1. Distribution of $[RhCl_n(H_2O)_{6-n}]^{3-n}$-species ($n = 0–6$) as a function of -pCl ($\log[Cl^-]$).

These formation constants (stability constants), for the following complexation reactions, were used to construct a distribution diagram for the Rh(III) chloro–aqua complexes as a function of pCl (Fig. 1).

$$[RhCl_{n-1}(H_2O)_{7-n}]^{4-n} + Cl^- \overset{\beta_n}{\rightleftharpoons} [RhCl_n(H_2O)_{6-n}]^{3-n} + H_2O,$$

$$(n = 1 - 6) \tag{8}$$
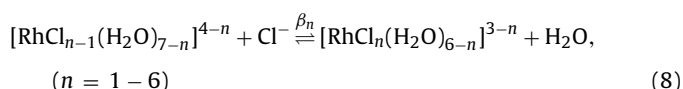
At the peak of each complex, coinciding with a fixed chloride concentration, the distribution (percentage values) of all complexes (in equilibrium with one another) can be determined (Fig. 1 and Table 2). From this it is evident that all complexes are dominant, to a greater extent, except for $[RhCl(H_2O)_5]^{2+}$, $[RhCl_2(H_2O)_4]^+$, and $RhCl_3(H_2O)_3$. Each solution, to be illuminated, was prepared at that specific pCl ($-\log[Cl^-]$) value that coincides with the maximum of each $[RhCl_n(H_2O)_{6-n}]^{3-n}$-species ($n = 0–6$). The required chloride concentration for each solution was obtained through the addition of NaCl (Tables 2 and 3). Due to the slow formation of the complexes the individual solutions were prepared by heating the solutions to 90 °C [10] for 10 h employing a Julabo F12 ED thermostatically controlled waterbath. These solutions were subsequently cooled to 25 °C, which was the temperature at which all photocatalytic reduction reactions were conducted. So as to ensure a constant ionic strength of unity for the illuminated solutions (where $n = 0–5$), the balance of the individual solutions was made up with $NaClO_4 \cdot H_2O$ (Tables 3 and 4). For the highest coordinated complex, i.e. $[RhCl_6]^{3-}$, it was however necessary to work at an ionic strength of 4.6 M to obtain a 65.4% presence of this species (Tables 2 and 4). Above this value NaCl would not dissolve completely for the given reaction volume of 500 ml and a temperature of 25 °C. A reaction solution of $RhCl_3 \cdot 3H_2O$ without addition of NaCl, but with $NaClO_4 \cdot H_2O$ for ionic strength adjustment to 1, was prepared from the stock solution and subjected to photocatalytic reduction for comparison purposes. The $HClO_4$ acid concentration, constant for each illuminated solution, was such that the pH of each solution was approximately 1.

With the distribution of the rhodium(III)-complexes known and fixed, the photocatalytic reduction trends of these complexes were investigated at those Cl^--concentrations that coincide with the maximum of each species.
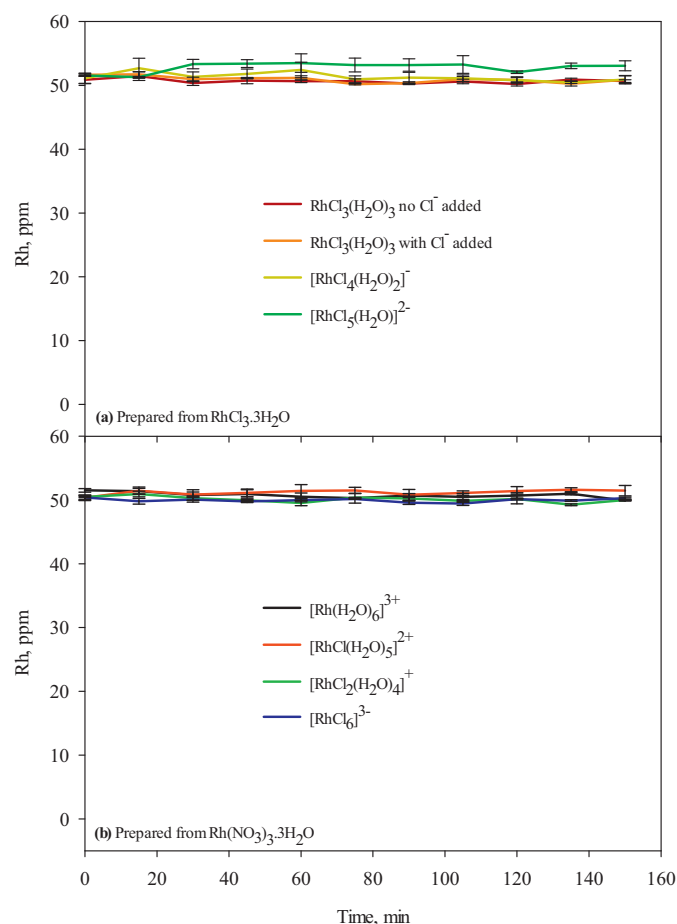
Fig. 2. Photocatalytic reduction of the $[RhCl_n(H_2O)_{6-n}]^{3-n}$-system for (a) $n = 3–5$, and (b) $n = 0–2, 6$ at 25 °C in air over a P25 TiO_2 (2 g l^{-1}) photocatalyst at pH 1, in the absence of an added SRA.

2.3. Experimental procedure and sample analysis

The experimental apparatus and procedure were the same as reported previously [19] with notable differences being the investigation of Rh(III) instead of Pd(II) chloro–aqua complexes and the additional use of organic SRAs in this study. The reaction suspensions were continuously stirred for 30 min in the dark, prior to illumination, to allow for maximum catalyst dispersion and equilibrium adsorption of reactants onto the TiO_2 photocatalyst surface. During a run of 150 min, 10 ml samples were taken from the reservoir at 15 min intervals and filtered twice, employing Whatman grade 42 filter paper. Analyses were conducted by means of inductively coupled plasma (ICP) emission spectroscopy employing a Thermo iCAP 6300 instrument. UV/vis spectra were recorded employing an Analytik Jena Specord S600 Diode Array spectrometer.

3. Results and discussion

Earlier studies [7,9] indicated that it is extremely difficult to photocatalytically reduce Rh(III) in TiO_2 suspensions without the addition of an added organic SRA. In those studies, as well as in the photocatalytic reduction of metal ions in general, the effect of metal speciation is hardly mentioned. The illumination of TiO_2 suspensions, under the prevailing conditions that would allow for cationic, neutral and anionic rhodium(III) complexes to be dominant in solution, in the absence of an added organic SRA, have however resulted in no photocatalytic reduction of any of the complexes (Fig. 2).

Table 2
Speciation of $[RhCl_n(H_2O)_{6-n}]^{3-n}$-system ($n = 0–6$) as a function of pCl at a constant pH and ionic strength.

pCl	$[Cl]^-$, M	$[Rh(H_2O)_6]^{3+}$(%)	$[RhCl(H_2O)_5]^{2+}$(%)	$[RhCl_2(H_2O)_4]^+$ (%)	$RhCl_3(H_2O)_3$(%)	$[RhCl_4(H_2O)_2]^-$ (%)	$[RhCl_5(H_2O)]^{2-}$ (%)	$[RhCl_6]^{3-}$ (%)
−0.60	4.60×10^0	0.000	0.000	0.000	0.022	2.544	32.032	**65.402**
0.00	1.00×10^0	0.000	0.000	0.012	0.582	17.186	**54.347**	27.873
1.00	1.00×10^{-1}	0.014	0.434	3.957	19.381	**57.198**	18.088	0.928
1.50	3.16×10^{-2}	0.784	7.665	22.107	**34.240**	31.955	3.195	0.052
2.00	1.00×10^{-2}	11.482	35.482	**32.360**	15.849	4.677	0.148	0.001
2.50	3.16×10^{-3}	43.349	**42.363**	12.217	1.892	0.177	0.002	0.000
8.50	0.00	**100.000**	0.000	0.000	0.000	0.000	0.000	0.000

Table 3
Adjustment of the ionic strength (I) to 1 M for the neutral and anionic solutions ($n = 3–5$) prepared from $RhCl_3 \cdot 3H_2O$.
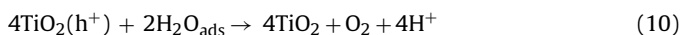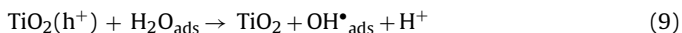
Rh(III) species	Rh^{3+} (mol l^{-1})	$HClO_4$ (mol l^{-1})	NaCl (mol l^{-1})	$NaClO_4 \cdot H_2O$ (mol l^{-1})	I (mol l^{-1})
$RhCl_3 \cdot 3H_2O$ (no Cl^- added)	4.86×10^{-4}	7.68×10^{-2}	0.00	0.921	1
$RhCl_3 \cdot 3H_2O$ (with Cl^- added)	4.86×10^{-4}	7.68×10^{-2}	3.02×10^{-2}	0.885	1
$[RhCl_4(H_2O)_2]^-$	4.86×10^{-4}	7.68×10^{-2}	9.85×10^{-2}	0.822	1
$[RhCl_5(H_2O)_2]^{2-}$	4.86×10^{-4}	7.68×10^{-2}	9.99×10^{-1}	0.000	1

Table 4
Adjustment of the ionic strength (I) for cationic complexes ($n = 0–2$) and for the anionic complex ($n = 6$) prepared from $Rh(NO_3)_3 \cdot 3H_2O$.
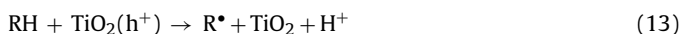
	Rh^{3+} (mol l^{-1})	NO_3^- (mol l^{-1})	$HClO_4$ (mol l^{-1})	NaCl (mol l^{-1})	$NaClO_4 \cdot H_2O$ (mol l^{-1})	I (mol l^{-1})
$[Rh(H_2O)_6]^{3+}$	4.86×10^{-4}	1.46×10^{-3}	0.10	0.00	0.40	1
$[RhCl(H_2O)_5]^{2+}$	4.86×10^{-4}	1.46×10^{-3}	0.10	3.16×10^{-2}	0.39	1
$[RhCl_2(H_2O)_4]^+$	4.86×10^{-4}	1.46×10^{-3}	0.10	1.0×10^{-1}	0.39	1
$[RhCl_6]^{3-}$	4.86×10^{-4}	1.46×10^{-3}	0.10	3.98×10^0	0.00	4.6

The photocatalytic reduction of two anionic rhodium(III) complexes, i.e. $[RhCl_4(H_2O)_2]^-$ and $[RhCl_5(H_2O)]^{2-}$, were compared to the photocatalytic reduction of the neutral $RhCl_3(H_2O)_3$ complex (with and without chloride added) as per speciation (Fig. 2a). The photocatalytic reduction of the anionic complex $[RhCl_6]^{3-}$, shown together with the cationic complexes as it was prepared from a $Rh(NO_3)_3 \cdot 3H_2O$ solution (Fig. 2b), did not reveal any photocatalytic reduction as well.

As the UV irradiation of these suspensions were carried out in the absence of an organic electron donor, in order to trap the positively charged valence band holes, it would imply that the only available SRA was either water in the bulk solution or water within the coordination sphere of the complexes with two possible oxidation pathways of H_2O (Eqs. (9) and (10), compare with the earlier case [19]). As no photocatalytic reduction occurs in the absence of an added SRA, the addition of easily oxidized sacrificial reducing agents (SRAs) is therefore required. Three structurally different organic SRAs were subsequently investigated, namely (a) formic acid, (b) ethanol, and (c) sucrose.

$$TiO_2(h^+) + H_2O_{ads} \rightarrow TiO_2 + OH^\bullet_{ads} + H^+ \tag{9}$$

$$4TiO_2(h^+) + 2H_2O_{ads} \rightarrow 4TiO_2 + O_2 + 4H^+ \tag{10}$$

The three SRA structures reveal that the ethanol and formic acid molecules have one oxidizable hydroxyl site each while the sucrose molecule has nine oxidizable sites. Formic acid only contains a single carbon atom, with ethanol having two and sucrose having multiple carbon atoms. Theoretically, sucrose is therefore expected to be a stronger SRA than ethanol and formic acid with the SRA, represented by RH in the following reaction scheme (Eqs. (11)–(14)), being oxidized to carbon dioxide, water and mineral acids via an intermediate OH radical (indirect, Eq. (12)) or a positive hole (direct, Eq. (13)) [21,26].

$$TiO_2(h^+) + OH^- \rightarrow TiO_2 + OH^\bullet \tag{11}$$

$$RH + OH^\bullet \rightarrow R^\bullet + H_2O \tag{12}$$

$$RH + TiO_2(h^+) \rightarrow R^\bullet + TiO_2 + H^+ \tag{13}$$

$$R^\bullet \rightarrow CO_2 + H_2O + mineral acids \tag{14}$$

The results of the photocatalytic reduction of the $[RhCl_n(H_2O)_{6-n}]^{3-n}$-system ($n = 3–5$) are shown in Fig. 3 with 0.01 M SRA added. The rate of reduction was fastest when $RhCl_3(H_2O)_3$ (with and without chloride added) and $[RhCl_4(H_2O)]^-$ dominate in solution with sucrose as SRA. Ethanol (at 0.01 M) also exhibited some activity as SRA for the reduction of the neutral and anionic chloro–aqua rhodium(III) complexes, although it was weaker than sucrose at the same concentration. No photocatalytic reduction was however observed when formic acid was used as SRA. With sucrose as SRA a unique shape for the reduction of $RhCl_3(H_2O)_3$ (with chloride added) and $[RhCl_4(H_2O)]^-$ is observed (Fig. 3). The 'plateau'-like shape at the onset of illumination can be taken as an induction period where sucrose is oxidized to produce more reactive intermediates that are better hole scavengers than the sucrose molecule itself. A study by Vamathevan et al. [27] concluded that in bare titania systems (without any metal doping) the degradation of sucrose was solely via a photo-oxidative pathway of the sucrose molecule by the photogenerated holes. Tran et al. [28] went further to observe that although sucrose has a limited adsorption capacity on TiO_2 the generated intermediates comprise of highly hydroxylated carboxylic acids that easily adsorb onto the photocatalyst and are readily attacked by the positive holes. Hence, the rate limiting step in the photocatalytic reduction of the anionic complexes is the generation of these intermediates. Ethanol's superior activity compared to that of formic acid as an SRA (at 0.01 M) could be attributed to the fact that ethanol is easily oxidized to acetic acid, a carboxylic acid, which, as just stated, easily adsorbs onto the TiO_2 surface and is subsequently oxidized to acetaldehyde, methanol and finally carbon dioxide [19]. There is therefore a long reaction pathway during which electrons can be 'extracted'. Formic acid, a carboxylic acid, does not have this long reaction pathway and is easily depleted. Sucrose has the longest reaction pathway and is therefore the strongest SRA under these conditions. The photocatalytic reduction of the neutral and anionic rhodium(III) chloro–aqua complexes exhibit the following decreasing order for both sucrose and ethanol as SRAs at 0.01 M: $RhCl_3(H_2O)_3$ (without chloride added) > $RhCl_3(H_2O)_3$ (with chloride added) > $[RhCl_4(H_2O)_2]^- \gg [RhCl_5(H_2O)]^{2-}$, with
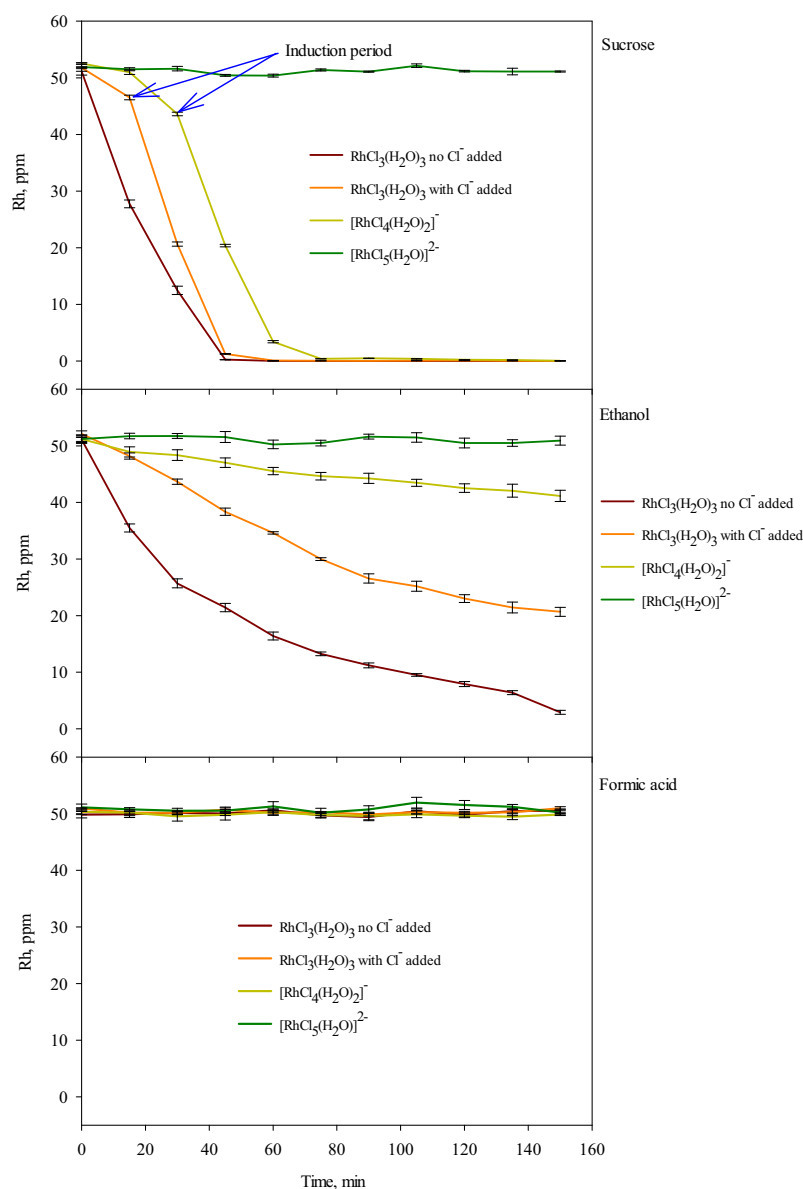
Fig. 3. Photocatalytic reduction of the $[RhCl_n(H_2O)_{6-n}]^{3-n}$-system ($n$ = 3–5) at 25 °C in air over a P25 TiO$_2$ (2 g l^{-1}) photocatalyst using 0.01 M of sucrose, ethanol and formic acid as SRAs at pH 1.

$[RhCl_5H_2O]^{2-}$ showing resistance to photocatalytic reduction at pH 1 (Fig. 3).

For similar work on the photocatalytic reduction of Hg(II), Wang et al. [29] found that the photocatalytic reduction rate significantly decreases with an increase in chloride concentration. The explanation for that observation was either (i) the presence of a mixture of different Hg(II) chloro–aqua complexes with different redox potentials, that would have different reduction rates, or (ii) the fact that higher chloride concentrations block the active sites of TiO$_2$ as its surface is positively charged in acidic conditions, thereby decreasing its activation by UV light. The photocatalytic reduction rate trend of the $[RhCl_6]^{3-}$ complex is expected to be similar to that of $[RhCl_5(H_2O)]^{2-}$ since their redox potentials are almost the same (Eqs. (6) and (7)). The cationic complexes and the $[RhCl_6]^{3-}$ complex did not reduce when 0.01 M sucrose was added (Fig. 4).

A possible reason why lower chlorinated species (cationic complexes) were not reduced at pH 1 (Fig. 4) might be due to their poor adsorptive interaction with the Evonik Degussa P25 TiO$_2$ surface, whic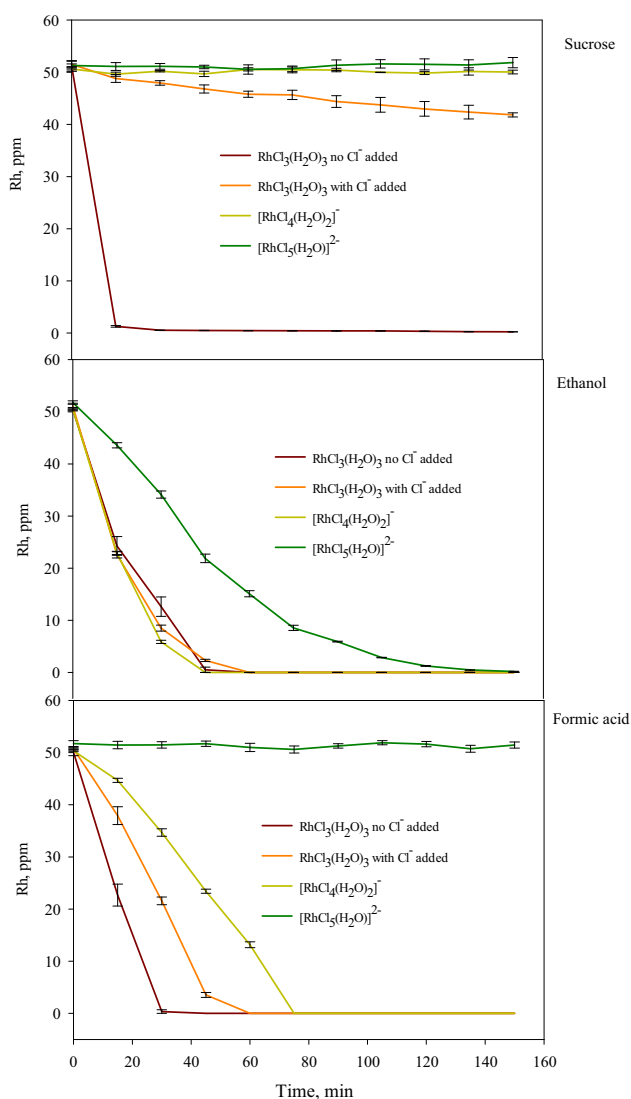h is known to be positively charged at pH values less than its isoelectric point of 7 [29]. From Figs. 3 and 4 it is clear that the negatively charged complexes are easily reduced while the positively charged complexes are not reduced although having a more favourable standard reduction potential (Eqs. (1)–(7)). The thermodynamic prediction of ease of reduction (Eqs. (1)–(3)) therefore dictates that the cationic complexes would be relatively easier to reduce than the neutral and anionic species. Since the pH of the solutions was kept constant at 1 for all the runs, the interaction of the cationic complexes and the photocatalyst was mutually repulsive.

In addition to employing sucrose at 0.01 M (Fig. 3) the photocatalytic reduction rate trends of $[RhCl_n(H_2O)_{6-n}]^{3-n}$-complexes ($n$ = 3–5) were also investigated at a higher concentration of 0.1 M (Fig. 5). At this concentration it is clear that ethanol is now a much more effective SRA compared to both sucrose and formic acid. The order of SRA effectiveness is now ethanol > formic acid > sucrose, at 0.1 M, compared to sucrose > ethanol > formic acid at 0.01 M. From Fig. 5 one can also see that, in the case of ethanol, a solution with the $[RhCl_5(H_2O)]^{2-}$ complex being predominant is now also reduced,
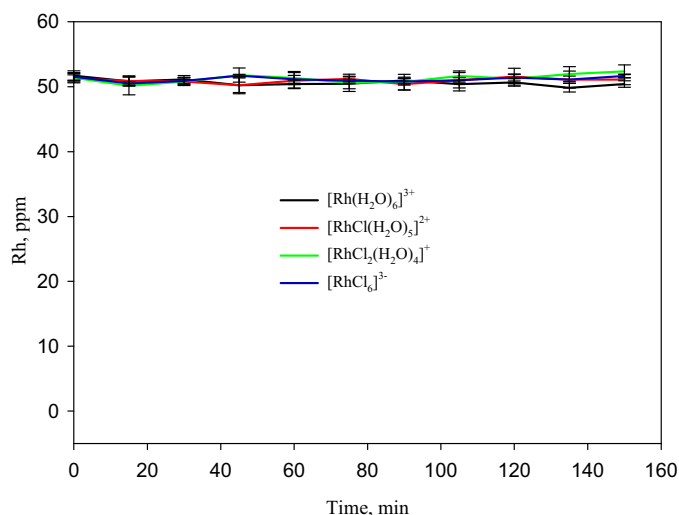
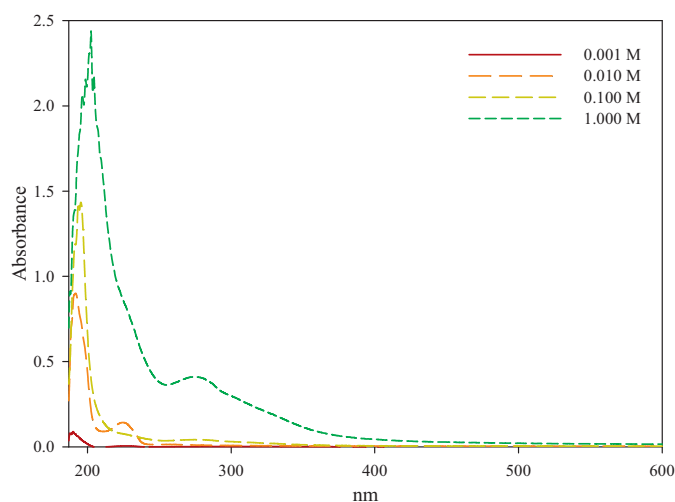**Fig. 4.** Photocatalytic reduction of the $[RhCl_n(H_2O)_{6-n}]^{3-n}$-system ($n = 0$–$2$) and ($n = 6$) at 25 °C using 0.01 M sucrose over a P25 TiO$_2$ (2 g l^{-1}) photocatalyst at pH 1.

Fig. 6. UV/vis absorbance spectra of different concentrations of sucrose.

Fig. 5. Photocatalytic reduction of the $[RhCl_n(H_2O)_{6-n}]^{3-n}$-system ($n = 3$–$5$) at 25 °C in air over a P25 TiO$_2$ (2 g l^{-1}) photocatalyst using 0.1 M of sucrose, ethanol and formic acid as SRAs at pH 1.

albeit slower than the other three anionic complexes, compared to when 0.01 M ethanol was used as SRA. Sucrose, at lower concentration (0.01 M), goes from being the most effective SRA to being the least effective SRA at higher concentration (0.1 M). This could be attributed to lower sucrose mineralisation as a study by Tan et al. [30] suggested that lower sucrose mineralisation was due to the formation of intermediates that block the active photocatalyst surface sites. Their study found formic acid to be a superior SRA than both sucrose and ethanol, which they attributed to its ability to simultaneously adsorb onto the TiO$_2$ surface with the complexes under investigation, which in their case were Se(IV) and Se(VI) ions. They found that increasing the concentration of both formic acid and ethanol resulted in an increase of the reduction of Se(IV) ions with formic acid outperforming ethanol. They, however, did not investigate the effect that a change in sucrose concentration has on the photocatalytic reduction of Selenium ions. From our results it is clearly evident that both sucrose and ethanol outperforms formic acid as hole scavenger towards the photocatalytic reduction of Rh(III) chloride ions whereas, according to the work done by Tan and co-workers [30] on Selenium, formic acid outperformed all other hole scavengers including sucrose and ethanol. It would therefore seem that hole scavengers (as sacrificial reducing agents) cannot be assigned an absolute strength, but that their perceived strength is directly linked to the system under investigation.

In an effort to probe whether or not sucrose in itself blocks the active photocatalyst surface sites of TiO$_2$, we investigated the UV absorbance of different concentrations of sucrose alone, i.e. 0.001 M, 0.01 M, 0.1 M and 1.0 M (Fig. 6). With a band gap of 3.2 eV Degussa P25 TiO$_2$ absorbs UV light below 383 nm [7]. The black-light fluorescent lamp employed emits UV light between 300 and 425 nm with a peak at 350 nm [7]. From Fig. 6 it is evident that sucrose starts absorbing UV light below 400 nm, at high concentrations, and at the lower concentrations we employed sucrose absorbs below 300 nm, with the bulk around 200 nm. Sucrose in itself should therefore not block TiO$_2$'s active surface sites. In an effort to prove this assumption solutions were made up containing a fixed amount of TiO$_2$, but with increasing amounts of sucrose. These solutions were made up at those concentrations coinciding with experimental conditions, but were found to be much too high as no usable UV absorbance spectra could be obtained. These original solutions had to be diluted a hundredfold so as to obtain respectable UV absorbance spectra (Fig. 7). It is evident that there is a marked difference in the UV absorbance spectra for the lower sucrose concentrations (smaller sucrose to TiO$_2$ ratios) compared to the higher concentration (higher sucrose to TiO$_2$ ratio) with the
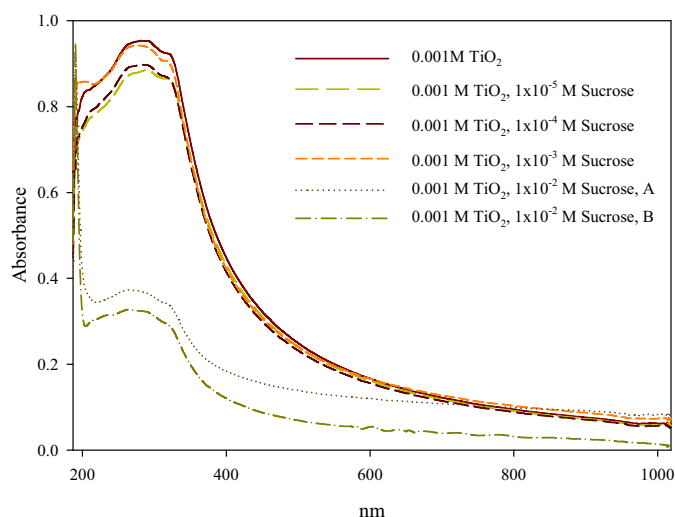
Fig. 7. UV/vis absorbance spectra of a fixed concentration of TiO$_2$ with varying concentrations of sucrose with A and B being repeats.

Fig. 8. Photocatalytic reduction of the [RhCl$_n$(H$_2$O)$_{6-n}$]$^{3-n}$-system ($n = 0$–2) and $n = 6$ at 25 °C using 0.1 M sucrose over a P25 TiO$_2$ (2 g l^{-1}) photocatalyst at pH 1.

solution containing the greatest amount of sucrose absorbing only about half as much UV light. This is directly attributed to the sucrose causing coagulation of the suspended TiO$_2$, which was observed in the original solutions made up at concentrations representing experimental conditions. Coagulation causes the TiO$_2$ to settle out and the decrease in photocatalytic activity at higher sucrose concentrations can therefore be directly attributed to there being less TiO$_2$ in suspension.

Comparing Figs. 3 and 5 one can see that when the neutral RhCl$_3$(H$_2$O)$_3$ complex (without chloride added) predominates in solution it is the fastest reducing species at both 0.01 M and 0.1 M sucrose concentration. There is no induction period observed for its reduction and it is reduced within 15 min for a sucrose SRA concentration of 0.1 M and within 45 min for a sucrose SRA concentration of 0.01 M, respectively. This may be explained by the fact that unlike the anionic complexes both its ligands (chloride and water) occur within the coordination sphere and there is no free chloride (in the bulk solution) to interfere with the substrate-photocatalyst interaction. As a result the water in the coordination sphere is able to act as SRA in synergy with sucrose. Chen [21] reported that if no organics are present in a photocatalytic reduction system, water gets oxidized by the photogenerated holes as shown in reaction 10 at which point the photocatalytic reduction of metal ions (in this case Rh(III)) may be limited by the low rate of water oxidation. Since no photocatalytic reduction of RhCl$_3$(H$_2$O)$_3$ complex (without Cl$^-$ added, Fig. 2) was observed, in the absence of an added organic SRA, one can conclude that, although the electrochemical redox reaction of water is thermodynamically feasible (according to Eqs. (10) and (15)) it is nonetheless a four electron kinetically slow process, which competes with the recombination of electron–hole pairs on the surface of the photocatalyst [21]. Moreover, under acidic conditions the hydroxide product (Eq. (15)) will be highly unlikely. Hence, a stronger external hole scavenger (SRA) in the form of an organic compound is necessary to maintain charge separation and promote the photocatalytic reduction of the neutral rhodium(III) chloro–aqua complex.

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad 0.401(E^\circ(V)) \tag{15}$$
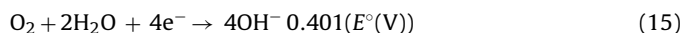
As for the photocatalytic reduction of the cationic and the highly chlorinated [RhCl$_6$]$^{3-}$ complexes at 0.1 M sucrose SRA concentration (Fig. 8), again no reaction was observed for the same reasons as already mentioned in the section above where 0.01 M SRA concentrations were used. Only sucrose was investigated for the
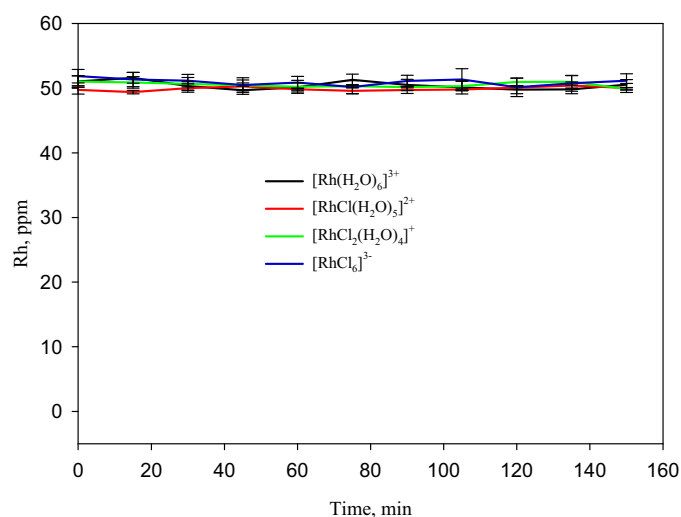
photocatalytic reduction of the cationic and the highly chlorinated [RhCl$_6$]$^{3-}$ complexes because it showed higher hole scavenging activity at low concentrations and the objective of this method is to use as little organic SRA as possible. From an industrial metal recovery point of view more test runs were carried out on the anionic than cationic complexes [1,12].
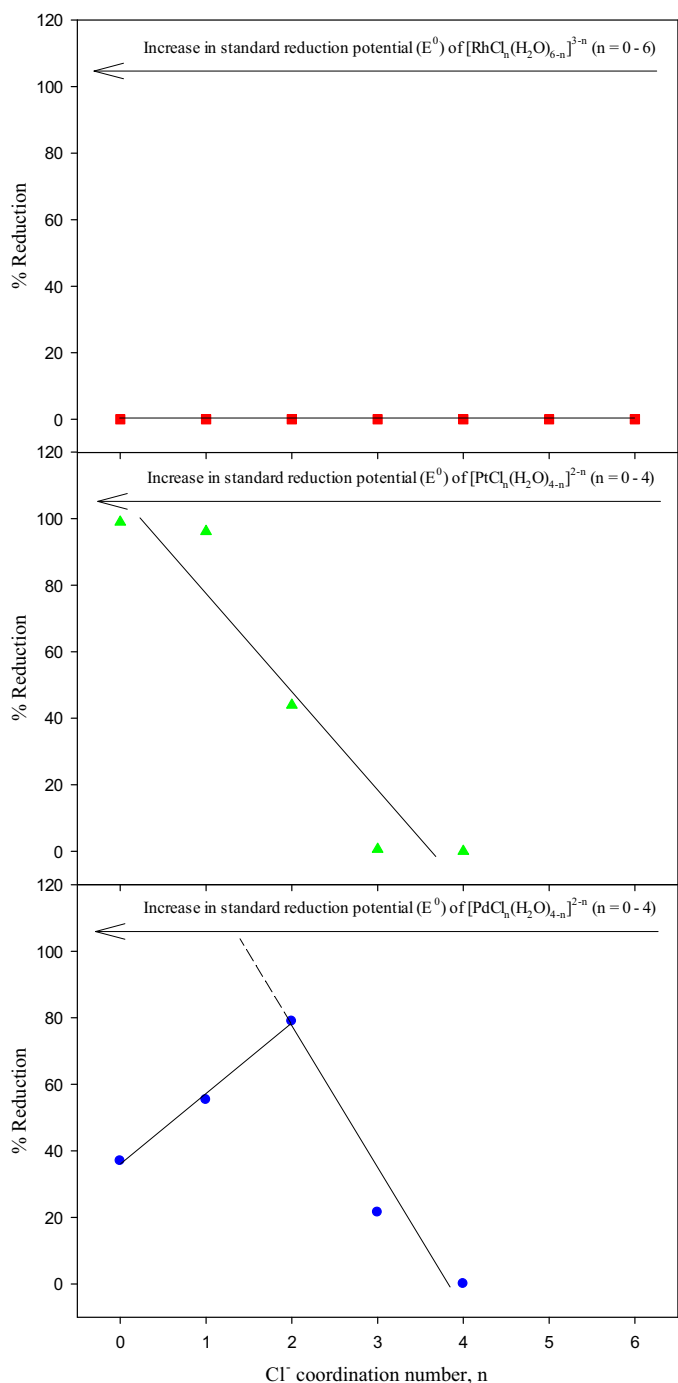
The results of experimental blank runs on RhCl$_3$(H$_2$O)$_3$ with or without NaCl added according to speciation (because they were the fastest reducing in the presence of an added SRA) were carried out to ascertain whether adsorption and/or photolysis occurred. Both complexes did not reduce in the absence of either UV illumination (TiO$_2$ only) or TiO$_2$ (UV illumination only) in the presence of 0.1 M ethanol. The driving force for the photocatalytic reduction process was, therefore, the combined effect of UV light and TiO$_2$, i.e. a photocatalytic process.

Comparing the photocatalytic reduction of [RhCl$_n$(H$_2$O)$_{6-n}$]$^{3-n}$ ($n = 0$–6) to that of [PdCl$_n$(H$_2$O)$_{4-n}$]$^{2-n}$ ($n = 0$–4) [19] and [PtCl$_n$(H$_2$O)$_{4-n}$]$^{2-n}$ ($n = 0$–4) [20], in the absence of an added sacrificial reducing agent, a marked difference is observed (Fig. 9). The chloride complexes of Pd(II) and Pt(II) all reduce except for the four coordinated complex ($n = 4$), in both cases. In contrast none of the Rh(III) complexes reduce in the absence of an added organic sacrificial reducing agent. If one compares the standard reduction potentials (E° (V)) of these complexes it would seem that complexes with E°-values above 0.650 V, from the 'perspective' of Pd(II), would be able to reduce photocatalytically (Table 5). This should mean that [Rh(H$_2$O)$_6$]$^{3+}$, [RhCl(H$_2$O)$_5$]$^{2+}$, and [RhCl$_2$(H$_2$O)$_4$]$^+$ all stand a chance to be reduced. However, from the 'perspective' of Pt(II),

Table 5
Standard reduction potentials, E° (V), for the chloride complexes of Pd(II), Pt(II) and Rh(III) (√, reduced in the absence of an SRA; ×, not reduced in the absence of an SRA).

n	E° (V)		
	[PdCl$_n$(H$_2$O)$_{4-n}$]$^{2-n}$ [19]	PtCl$_n$(H$_2$O)$_{4-n}$]$^{2-n}$ [20]	[RhCl$_n$(H$_2$O)$_{6-n}$]$^{3-n}$
0	0.951 √	1.008 √	0.758 ×
1	0.819 √	0.970 √	0.708 ×
2	0.721 √	0.852 √	0.670 ×
3	0.650 √	0.769 √	0.637 ×
4	0.610 ×	0.710 ×	0.608 ×
5	–	–	0.598 ×
6	–	–	0.604 ×

Fig. 9. Observed photocatalytic reduction rate trends of Pd(II) [19], Pt(II) [20] and Rh(III) chloro–aqua complexes within 15 min of illumination in the absence of an added organic SRA.

hole) could very well play a role in determining the rate of photocatalytic reduction. It is therefore a combination of all these factors, i.e. the standard reduction potential, the interaction of the complex with the photocatalyst surface, and the oxidation of bound water molecules, that will determine whether or not any of the $[RhCl_n(H_2O)_{6-n}]^{3-n}$ ($n = 0$–6) complexes will be photocatalytically reduced or not, and at what rate.

4. Conclusions

The recovery of platinum group metals from solution is important as a means of waste water purification as well as a way of recovering and recycling these valuable metals. In this paper, the recovery of rhodium from its chloro–aqua complexes by photocatalytic reduction was explored. It has been shown that the rate of photocatalytic reduction of Rh(III) is directly linked to the dominant species in solution as well as to the nature and concentration of the sacrificial reducing agent (SRA). In contrast to the chloride complexes of Pt(II) and Pd(II) the presence of an organic SRA is required before any Rh(III) will be photocatalytically reduced. At low concentrations sucrose is a more effective SRA than both ethanol and formic acid in photocatalytically reducing neutral and anionic chloro–aqua rhodium(III) complexes. At high SRA concentrations ethanol outperformed both sucrose and formic acid due to coagulation and subsequent removal of the photocatalyst (TiO_2) from suspension. Formic acid with its "easily" oxidizable molecular structure did not prove to be the best SRA for this system and no absolute strength can be assigned to a SRA, as the strength of a SRA would seem to be linked to the system under investigation.

Acknowledgement

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complexes with $E°$-values somewhere below 0.769 V would not be able to reduce, which means that none of the Rh(III)-chloride complexes would reduce, which is indeed what is observed.

As is clear for the $[PdCl_n(H_2O)_{4-n}]^{2-n}$ ($n = 0$–4) system, it is not only the reduction potential of each complex that would determine whether or not the complex would reduce or not, and at what rate, as there is a marked difference between the observed reduction rate and the expected reduction rate based purely on the reduction potentials of the different Pd(II)-complexes (Fig. 9). How the complex interacts with the photocatalyst surface as well as the oxidation of in-sphere coordinated water molecules (by the positive

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